

# Marine Climate Archives and Geochemical Proxies: a Review and Future Investigations on the Mediterranean Sea

P. Montagna<sup>1,2</sup>, M. Taviani<sup>1</sup>, S. Silenzi<sup>3</sup>, M. McCulloch<sup>4</sup>, C. Mazzoli<sup>5</sup>, S. Goldstein<sup>1</sup>, R. Rodolfo-Metalpa<sup>6</sup>

1, Institute of Marine Sciences, CNR, Bologna, Italy

2, Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, U.S.A.

3, Institute for Environmental Protection and Research, Roma, Italy

4, The UWA Ocean Institute and School of Earth and Environment, Perth, Western Australia

5, Department of Geosciences, University of Padova, Italy

6, International Atomic Energy Agency, Environment Laboratories, Monaco, Principality Of Monaco

montagna@ldeo.columbia.edu

## Abstract

Paleoclimate research based on the investigation of geochemical proxies in marine climate archives has been growing considerably during the last two decades, due to the development of more precise analytical systems. Thermal ionization and inductively coupled plasma mass spectrometers, equipped with multi-collectors, enable to obtain precise and accurate isotopic data, an essential requirement for reliable reconstructions of the physical and chemical marine parameters. In the last 5 years, part of the paleoclimate investigation focused on the Mediterranean has been carried out using these cutting-edge analytical techniques through international collaborations among Italian, Australian and American scientists. Specimens of shallow- and deep-water corals collected in the Mediterranean Sea, in the Atlantic and Pacific Oceans, have been analysed with laser ablation and solution ICP-MS and with a thermal ionization mass spectrometer. The correlation between Li, Mg, P, normalized to Ca, and the Nd and B isotopic composition of the coral skeletons with the most important marine parameters has enabled to develop and validate new geochemical proxies. The derived calibration equations can now be applied to well-dated fossil corals with the aim to reconstruct the climate variations in the past.

This article reviews some of the principal results achieved in the last 5 years by the authors and present some future directions on the application of geochemistry to coral investigation.

## 1 Introduction

Considerable effort has been made in recent years to refine and develop geochemical proxies in coral skeleton as reliable

tools for Late Quaternary paleoclimate reconstructions of important marine parameters, such as temperature, salinity, nutrient content and pH evolution [1, 2, 3, 4, 5, 6].

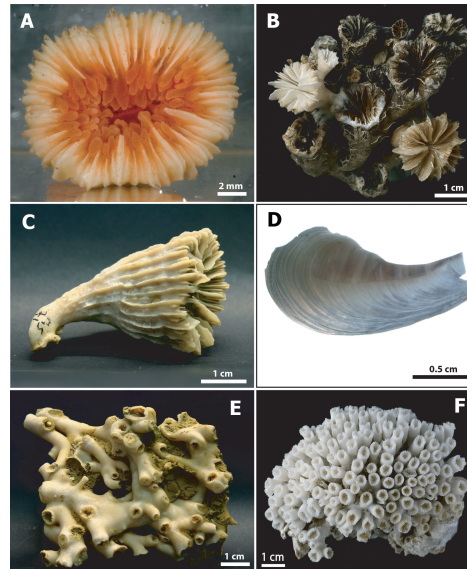


Figure 1: Shallow and deep-water corals collected in the Mediterranean Sea. A. Distal view of the calyx of a live *Desmophyllum dianthus* showing the orange tentacles and the septa. B. Fossil *D. dianthus* colonized by sub-recent and live specimens of the same species. C. Distal-lateral view of a 37kyrs old *D. dianthus*. D. Transmitted light image of the main septum (S1) of a *D. dianthus*. White and dark microbands form the density banding characteristic of this species. E. 48kyrs old *Lophelia pertusa* colony retrieved in the Strait of Sicily. F. *Cladocora caespitosa* subspherical colony from Miramare in the Northern Adriatic Sea. Colony is characterized by distinct corallites, each having its own wall, growing in a continuous rectilinear way.

Due to their carbonate mineralogy, corals can be precisely dated by means of AMS  $^{14}\text{C}$  and mass spectrometric U/Th dating [7, 8], and they systematically incorporate trace elements and stable isotopes, thus being capable to provide multi-century, sub-annual resolution records. Since the interpretation of coral geochemistry is complicated by the overprinting of physiological processes of skeletal formation, more emphasis has been placed to better understand the mechanisms of elemental uptake and isotopic fractionation, in order to retrieve reliable climatic and oceanographic

data from coral geochemistry (see [9], for a review).

Recent investigations on the trace elements and stable isotopic composition of the aragonitic exoskeleton of Mediterranean shallow and deep-water corals (Figure 1) have proved that different corals species thriving in the Mediterranean Sea at different depths in the water column can serve as climate archives [10, 11, 5, 6, 12].

Spatially-resolved geochemical measurements of lithium, boron, magnesium, phosphorus, calcium, strontium and uranium have been carried out on the skeleton of the

shallow-water coral *Cladocora caespitosa* and the cold-water coral species *Lophelia pertusa*, *Madrepora oculata*, *Desmophyllum dianthus*, and *Caryophyllia smithii* using a high-resolution laser ablation ICP-MS. This analytical technique allows the analysis of minor and trace elements at fine-scale resolution, in order to geochemically characterize the different microstructures comprising the coral skeleton.

The centres of calcification are considered to be the first component formed in the skeleton and are composed of tiny crystals surrounded by fibrous aragonitic bundles, which represent the bulk of the skeleton. Both coral microstructures show characteristic elemental and isotopic patterns, which might alter the interpretation of the environmental signals if not properly taken into account. On the basis of previous results at fine-scale resolution, we decided to focus on specific geochemical ratios (i.e. Li/Mg) that seem to overcome the bias related to the vital effect, giving a unique opportunity to retrieve precise information on the evolution of seawater temperature in the past. Very recently, there has been a growing interest in investigating non-traditional isotopic systems, such as neodymium and boron, in coral skeletons, with the aim to further our knowledge on the water mass dynamics and the pH evolution. Given the analytical difficulties in obtaining reliable Nd and B isotopic data in coral skeletons only few studies have been conducted so far [13, 14, 13]. The necessary precision for paleoclimate investigations required the use of more precise and accurate analytical machines, such as multi-collectors spectrometers, either with inductively coupled plasma or thermal ionization sources.

Here we briefly review some of the main results that we have obtained during the last five years in studying the geochemi-

cal composition of Mediterranean shallow and deep-water corals with an emphasis on temperature and nutrient sensitive elements. In addition, we present some of the new frontiers in coral geochemistry and the application of these new promising proxies in retrieving paleoclimate data for the Mediterranean Sea.

## 2 The Mediterranean sea: a natural laboratory for studying climate change

Due to its peculiar geographic position, situated at the boundary between the subtropical and mid-latitudes zones and its water mass dynamics, the Mediterranean Sea can be considered a perfect natural laboratory to understand the effects of climate changes on marine environment from the photic to the bathyal zone. The Mediterranean Sea is a semi-enclosed basin with an “anti-estuarine” circulation: the Atlantic water enters through the Strait of Gibraltar as surface water and it progressively becomes denser while flowing eastward through the Strait of Sicily towards the Levantine basin. In the northern Levantine basin the Modified Atlantic Water sinks to form the more saline Levantine Intermediate Water (LIW), which represents the major constituent of the Mediterranean Intermediate Water and part of the Mediterranean Outflow into the Atlantic Ocean. The LIW flows westward from the Eastern basin between 150 and 600 meter water depth via the relatively shallow Strait of Sicily (see [15], for a review). During wintertime the effect of atmospheric cooling and evaporation produce cold dense waters that cascade off the continental shelf in specific locations of the Mediterranean Sea

such as in the Gulf of Lions, in the Southern Adriatic Sea and in several Aegean shelves. This process forms the deep water system of the Mediterranean Sea, a relevant but still poorly known component of the entire basin. Even though this is a very simplistic view of the Mediterranean circulation it gives an idea of the complexity of the Mediterranean dynamics, characterized by a general circulation typical of the open ocean. All these basin scale features were and are impacted by climate change and the investigation of some of the most important physical and chemical parameters, such as sea water temperature, nutrient contents and the state of the ventilation, in the past can help to further elucidate the climate evolution and the processes operating in the basin. The Mediterranean Sea behaves as a “miniature ocean” [16], with contrasting water masses flowing from the Eastern to the Western basins and viceversa, therefore representing an ideal case-study for building up our knowledge not only on the internal Mediterranean dynamics but also on the climate changes on a global scale. The Mediterranean seems to respond faster than the open oceans to climate variations and this gives the unique opportunity to study the effects of the climate change at a shorter time-scale using the coral geochemistry.

### 3 Previous geochemical studies of Mediterranean corals for paleoclimate reconstructions

Previous studies on the geochemical composition of shallow and deep-water coral skeletons from the Mediterranean Sea have

been mainly focused on the development of geochemical proxies for the seawater temperature and the nutrient content reconstruction of the water column [10, 5, 6]. Silenzi et al. [10] analysed for the first time the geochemical composition of the zooxanthellae-bearing coral *Cladocora caespitosa*, a species living between 5 and 40 meters water depth and one of the most important marine biocostructural organisms in the Mediterranean Sea [17]. The Sr/Ca composition of the high-density bands, which represent part of the exoskeleton forming during the wintertime, was found to be significantly correlated to the winter sea surface temperature (SST), providing the first calibration equation. Montagna et al. [6] refined the Sr/Ca equation using a laser ablation ICP-MS on a living coral collected in the Northern Adriatic Sea. In addition, a suite of elements, such as Li, B, Mg, P, Ca and U were analysed at fortnightly resolution. A new set of calibration equations were derived between B/Ca, Mg/Ca and U/Ca against SST. The results proved that this Mediterranean species can serve as a reliable recorder of the SST, although the “vital effect” can influence the elemental uptake (see below). At present, several samples from different locations in the Mediterranean Sea are being geochemically studied using bulk solution and laser ablation ICP-MS with the aim to produce precise calibrations to be applied to the fossil records.

An extensive review of these results can be found in Montagna et al. [12].

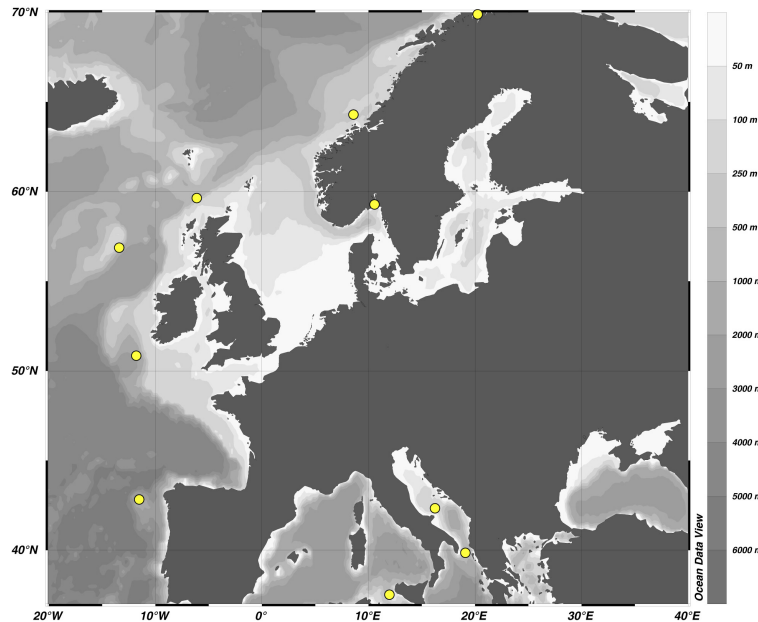


Figure 2: Sampling locations of the live *Lophelia pertusa* specimens used for Li/Mg measurements.

## 4 New frontiers in coral geochemistry

In the following pages we will discuss some of the new developments in coral geochemistry and the application of these new promising proxies in reconstructing the seawater temperature, the nutrient content, the water dynamics and the pH evolution of the Mediterranean Sea from the photic zone to the bathyal environment.

### 4.1 P/Ca ratios in the skeleton of deep-water corals: a proxy for seawater nutrient chemistry

The knowledge of the past seawater concentration of phosphorus, one of the ma-

ior bio-limiting nutrient, is important to estimate the contribution of the “biological pump” to the levels of atmospheric CO<sub>2</sub>. Therefore, evaluating past changes in the export of biological production to deep waters is a major issue. Unfortunately, most of the geochemical proxies used to quantify the seawater paleo-phosphorus concentration suffer to varying degrees of additional environmental factors, which potentially complicate the paleoceanographic reconstructions. We developed for the first time a direct method to reconstruct seawater paleo-phosphorus concentration by analysing the P/Ca encoded in the skeletal aragonite of the deep-sea coral species *Desmophyllum dianthus* [5]. The measurements were performed using a laser ablation ICP-MS and the beam was focused on the outer face of the main septum (Fig-

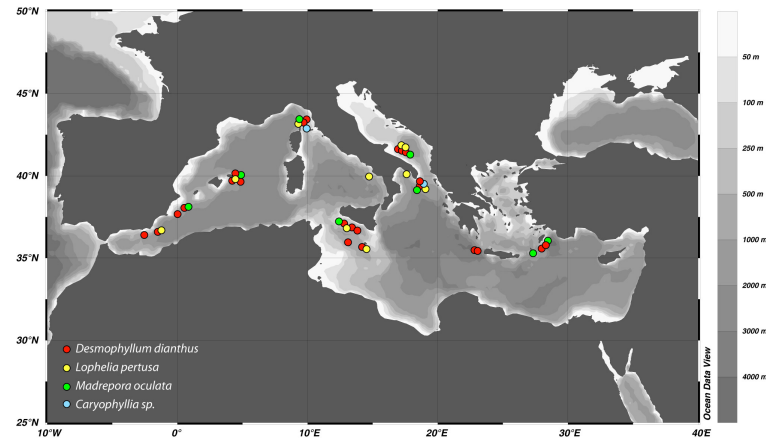


Figure 3: Map of the Mediterranean Sea with the sites where fossil deep-water corals are already available for geochemical investigations. Most of these samples have been U/Th dated with ages spanning the last ca. 500kyrs.

ure 1). A calibration equation was derived through the correlation between the coral P/Ca ratios of several specimens collected worldwide from a range of geographic locations and the corresponding dissolved inorganic phosphorus (DIP) concentration. The application of this equation to precisely dated fossil corals allowed us to characterize the trophic state of the intermediate water in the Western Mediterranean Sea at the end of the Younger Dryas period. Further fine-scale investigations enabled to improve the previous P/Ca vs. DIP equation, taking into account the presence of micro-size domains likely enriched in micro-apatite [18].

This proxy still represents the only direct method available so far to obtain information on the phosphate content of individual water masses in the past. Given the right fossil samples, the coral P/Ca proxy allows to quantify the fluxes of nutrients to intermediate and deep-water environments. Moreover, it can be used to reconstruct the

past ocean productivity, thereby furthering our understanding of the biological functions of the Mediterranean Sea in regulating atmospheric CO<sub>2</sub>.

#### 4.2 Li/Mg ratios in scleractinian corals: a new precise paleothermometer

Sensitive elements used in corals suffer to varying degrees of limitations due to physiological processes [19, 20, 21, 22, 23]. The coral physiology is actively controlling the chemical composition of different portions of the skeleton, and the temperature reconstructions are often complicated and biased by the overprint of this “vital effect”, likely related to the differential skeletal growth rate.

Very recently, the authors of the present contribution carried out a detailed geochemical study of the skeletal aragonite of shallow and deep-water corals, both in the field and in aquaria. By focusing a laser ab-

lation system on different skeletal portions of living samples of *Cladocora caespitosa* and *Lophelia pertusa* (Figure 2), we found that the distribution of most of the elements analysed, including Li, B, Mg, Sr and U is microstructure-related and largely depends on the different calcification mechanisms between the centres of calcification and the fibrous aragonite [24]. If these fine-scale variations translate into temperature, they provide a temperature range between 10 and 18°C, depending on the proxy and the calibration applied. Clearly, the chemical composition of the coral skeleton is not primarily controlled by the small temperature fluctuations in deep ocean sites, which are on the order of  $\pm 2^\circ\text{C}$  at most. In addition, we found that this micron-size scale heterogeneity is ubiquitous among different coral species, both zooxanthellate and azooxanthellate, implying similar physiological processes during the skeletogenesis [24]. For the first time we investigated the possibility of deconvolving environmental from physiological effects by analysing Li, Mg and Ca. Lithium and magnesium are highly correlated in shallow and deep-water corals and both seem to be similarly affected by the coral physiology. In order to correct for this “vital effect” Li/Ca ratios have been normalized for Mg/Ca ratios, providing a positive and highly significant correlation with the in-situ water temperature and suggesting a pure temperature control on Li/Mg ratio. Regardless of the exact mechanism that controls the uptake of Li and Mg, it seems clear that we can significantly improve the seawater temperature reconstructions with a precision of  $\pm 0.8^\circ\text{C}$  and with a particular sensitivity at low temperature such as those found in the deep ocean.

### 4.3 Nd-isotopes in deep-water corals as a novel ocean water mass tracer

At present, the main paleo-circulation tracers used in paleoceanography are stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of dissolved inorganic carbon and Cd/Ca in foraminifera, sortable silt,  $^{231}\text{Pa}/^{230}\text{Th}$  ratios and radiocarbon. Unfortunately, all these proxies are subject to limitations and vary as a function of additional biological and environmental factors, including remineralization, biological productivity and air-sea gas exchange.

Nd isotopes have been shown to be a promising new proxy to trace provenance and water mass mixing, being not fractionated by biological processes in the water column.  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios vary in the Earth as a result of  $\beta$  – decay of  $^{147}\text{Sm}$ , and in the ocean the values reflect the age of the continental sources of dissolved Nd, acting as a fingerprint of the dissolved Nd source regions. Since the residence time of Nd in the ocean is in the order of 500–1000 years [25], it can be effectively used as a tool to reconstruct the movement of water masses. This proxy has been successfully applied on marine cores, in the dispersed authigenic ferromanganese oxide precipitated in sediments [26, 27, 28], on foraminiferal shells [29] and on fossil fish teeth [30]. Only very recently, deep-water corals have been tested for their Nd-isotopic composition, showing a close relationship with the composition of the ambient seawater [31, 32], and opening new possibilities to obtain water mass signals and quantify mixing of water masses via paired neodymium isotopes and radiocarbon analyses of absolutely dated (U/Th) fossil corals.

The landmasses bordering the Mediter-

anean Sea have a distinct Nd-isotopic composition and this makes it possible to distinguish between different regional inputs [25, 33, 34, 35]. In particular, the Western Mediterranean Sea is characterized by Atlantic values entering the Mediterranean through Gibraltar whereas the Eastern basin displays more radiogenic values reflecting the input of major river such as the Nile [33].

The study of the Nd-isotopic composition of deep-water corals collected in strategic areas of the Mediterranean Sea (e.g. the Strait of Sicily) will provide a unique opportunity to investigate the modification of the Mediterranean circulation in the past in relation to climate change variations. Several living deep-water coral species (*Lophelia pertusa*, *Madrepora oculata*, *Desmophyllum dianthus* and *Caryophyllia smithii*) have been collected during a recent ISMAR-CNR cruise (MEDCOR cruise) in the Strait of Sicily at different depths in the water column, together with seawater samples. These samples will provide a unique opportunity to precisely calibrate the Nd-isotopic composition of the aragonite exoskeleton with the ambient seawater. They will also increase the extensive CNR collection of Mediterranean deep-water corals already available for geochemical studies (Figure 3), and most of which already U/Th and AMS  $^{14}\text{C}$  dated. Modern calibration experiments are essential to test a geochemical proxy that will be subsequently applied to the fossil coral collection. The Nd-isotopic signals of dated corals will be combined with more traditional tracers, such as radiocarbon, obtained from the same specimen in order to trace water provenance, mixing and rates of overturning circulation within the Mediterranean Sea during the Late Quaternary. Finally, those data may be further used to better

constrain reservoir effects for  $^{14}\text{C}$ -dating of marine benthic organisms.

#### 4.4 Reconstructing the seawater pH evolution in the Mediterranean Sea using boron isotopes in corals

pH is an important marine parameter that enables to evaluate part of the ocean carbonate system. As a result of human activity the ocean uptakes more  $\text{CO}_2$ , which leads to a drop in pH, a process called “Ocean acidification”. To better understand the future impact of ocean acidification in the Mediterranean Sea, in terms of physical, chemical and biological properties, long-term continuous seawater pH records are needed. Unfortunately, very little is known about the present-day pH variability in the Mediterranean Sea and paleo-pH data are completely missing (CIESM, 2008). Recently, it has been suggested that the analysis of boron isotopes in calcifying organisms can provide accurate seawater pH reconstructions [36]. The theory behind the B-isotopes as pH proxy is quite well established and is based on relatively simple equations. In aqueous solutions boron exists as two species, boric acid and borate ion, with the proportion of the two species being pH dependent. The two species show large isotopic fractionation ( $\sim 20\text{‰}$ ) due to different B-O vibrational energy and molecular geometry [37]. Since only the borate ion is postulated to be incorporated into marine carbonate [38], and given that the proportions of the aqueous species change according to pH, the boron isotopic composition in marine carbonate should also be a function of the ambient seawater pH during calcification [39]. While B-isotopes have been mainly mea-



sured on foraminiferal shells to reconstruct paleo-seawater pH at glacial-interglacial scale [40, 41, 42], investigations on corals are still in their infancy, with only a few calibrations undertaken using cultured corals [43, 44] and three reconstructions using modern long-lived [4, 45] and mid-late Holocene corals [46]. These first studies are very promising, indicating that the boron isotopic composition in corals actively responds to changes of the ambient seawater pH, with a precision better than  $\pm 0.02$  pH units [45]. However, pH reconstructions seem to be potentially affected by the coral microstructures (i.e. centers of calcification and fibrous aragonite) [47, 15], and further studies are essential to determine the exact mechanisms controlling the B-isotopes variations in corals. Very recently, we used positive thermal ionization mass spectrometry to analyse the B-isotopic composition of two *C. caespitosa* colonies cultured for one year under two different pCO<sub>2</sub> conditions: ambient pCO<sub>2</sub> (ca. 400  $\mu$ atm) and elevated pCO<sub>2</sub> (ca. 700  $\mu$ atm). The results clearly support the evidence that the B-isotopic composition of this coral species is pH-dependent and open new perspectives in reconstructing the paleo-pH evolution in the Mediterranean Sea using long-lived *C. caespitosa* colonies [48].

## 5 A geochemical multi-proxy approach for reconstructing the paleoclimate in the Mediterranean Sea

The advantage of coral skeletons in reconstructing the environmental parameters in

the past is represented by the possibility to combine a series of geochemical proxies obtained from the same precisely dated specimen. As stated before, scleractinian corals can incorporate a suite of minor and trace elements in their aragonite exoskeleton and they can be precisely dated by U/Th and AMS <sup>14</sup>C methods. In addition, compared to sediment cores, which are often affected by bioturbation, corals offer a continuous and usually undisturbed record of the Late Quaternary. If suitably calibrated, the different geochemical proxies can be combined together to reconstruct in detail the paleo-circulation of the Mediterranean Sea and its physical and chemical state through time. Until now, due to the lack of the proper samples and precise and accurate analytical techniques it has been difficult to reliably reconstruct the paleoclimate in the Mediterranean Sea at high-resolution. This novel multi-component approach will enable to answer specific paleoclimatic questions: How sensitive was the Mediterranean Sea to climatic events occurring during the last glacial and interglacial cycles in the Northern Hemisphere? How did the input/output water fluxes change through the sills, such as the Strait of Sicily? How did the Mediterranean circulation regime and the long term variability in the surface and deep layers change during the time? In the recent past the circulation of the Eastern Mediterranean Sea undergone a drastic change with the Aegean Sea replacing for some years the previously dominating Adriatic Sea as the main source of the Eastern Mediterranean Deep Waters (EMDW). This unique event is termed the Eastern Mediterranean Transient (EMT) and the real causes are still unknown although several hypotheses have been proposed [49]. This type of circulation changes might have also occurred dur-

ing previous periods and it is important to document these variations and investigate the link with the climatic events. These aspects remain largely unknown and one way to better understand the possible causes behind those changes is the detailed study of the coral geochemistry.

## 6 Conclusions

Shallow and deep-water corals from the Mediterranean Sea represent useful tools for the reconstruction of some of the most important marine parameters, such as seawater temperature, nutrient content, pH variations, seawater composition and water mass variability. Previous studies on the geochemical composition of living specimens of *Cladocora caespitosa* collected in the Mediterranean Sea revealed a strong correlation between Sr/Ca and B/Ca ratios with sea surface temperature [10, 6]. A refined study of the fine-scale geochemical pattern of *C. caespitosa* and the deep-water corals *Lophelia pertusa* enabled to identify a new promising temperature proxy (Li/Mg), which is independent of the vital effect, serving as a good candidate to reliably estimate temperature variations in the past.

More precise and accurate analytical techniques, such as multi-collector ICP-MS or TIMS, can now be employed for the investigation of B and Nd-isotopes in corals. First results of the boron isotopic composition of scleractinian corals seems to re-

flect the ambient seawater pH during the calcification process. This is very promising for the reconstruction of the paleo-pH variability at different depths in the water column and for the understanding of the carbonate system. The Nd-isotopic composition of deep-water corals has been shown to be directly related to the ambient seawater composition. Based on this finding, Nd-isotopes can be used to reconstruct the water mass dynamics, being able to track the different water masses.

We now dispose of several powerful geochemical tracers and proxies that, combined together, can be applied to precisely dated corals to reliably characterize the physical and chemical state of the Mediterranean Sea in the past.

## 7 Acknowledgements

We would like to thank the Captains, Officers, the Crew and shipboard staff of the many CNR coral cruises on-board RV Urania. This research benefited from financial support from ESF Euromargins/Eurocore "Moundforce", EU "Hermes", EU "Hermione", EU "MedatArchives", Firc "Aplabes" and Foundation Prince Albert II "COMP" projects. We are grateful to Alessandro Remia, Matthias López Correa, Lorenzo Angeletti, Alessandro Ceregato, Agostina Vertino and Helmut Zibrowius for great assistance during the various cruises. This is ISMAR scientific contribution n. 1724.

## References

- [1] T. Mitsuguchi, E. Matsumoto, O. Abe, T. Uchida, and P.J. Isdale. Mg/Ca thermometry in coral skeletons. *Science*, 274:961–963, 1996.
- [2] M.T. McCulloch, A.W. Tudhope, T.M. Esat, G.E. Mortimer, et al. Coral record

- of equatorial sea-surface temperatures during the penultimate deglaciation at Huon Peninsula. *Science*, 283:202–204, 1999.
- [3] M.K. Gagan, L.K. Ayliffe, J.W. Beck, et al. New views of tropical paleoclimates from corals. *Quaternary Science Reviews*, 19:45–64, 2000.
  - [4] C. Pelejero, E. Calvo, M.T. McCulloch, J.F. Marshall, et al. Preindustrial to modern interdecadal variability in coral reef pH. *Science*, 309:2204–2207, 2005.
  - [5] P. Montagna, M. McCulloch, M. Taviani, C. Mazzoli, and B. Vendrell. Phosphorus in cold-water corals as a proxy for seawater nutrient chemistry. *Science*, 312:1788–1791, 2006.
  - [6] P. Montagna, M. McCulloch, C. Mazzoli, S. Silenzi, and R. Odorico. The non-tropical coral *Cladocora caespitosa* as the new climate archive for the Mediterranean Sea: high-resolution (~weekly) trace element systematics. *Quaternary Science Reviews*, 26:441–462, 2007.
  - [7] A. Mangini, M. Lomitschka, R. Eichstadter, N. Frank, S. Vogler, et al. Coral provides way to age deep water. *Nature*, 392:347–348, 1998.
  - [8] H. Cheng, J.F. Adkins, R.L. Edwards, and E.A. Boyle. U-Th dating of deep-sea corals. *Geochimica et Cosmochimica Acta*, 64:2401–2416, 2000.
  - [9] A.L. Cohen and T. McConnaughey. Geochemical perspective on coral mineralization. *Review in Mineralogy and Geochemistry*, 54:151–187, 2003.
  - [10] S. Silenzi, E. Bard, P. Montagna, and F. Antonioli. Isotopic and elemental records in a non-tropical coral (*Cladocora caespitosa*): Discovery of a new high-resolution climate archive for the Mediterranean Sea. *Global and Planetary Change*, 49:94–120, 2005.
  - [11] P. Montagna, M. McCulloch, M. Taviani, A. Remia, and G. Rouse. High resolution trace and minor element compositions in deep-sea azooxanthellate solitary corals (*Desmophyllum dianthus*) from the Mediterranean Sea and the Great Australia Bight. In: Freiwald A, Roberts JM (eds) Cold-water Corals and Ecosystems. Springer, Berlin Heidelberg. 220:1109–1126, 2005.
  - [12] P. Montagna, M. McCulloch, C. Mazzoli, M. Taviani, and S. Silenzi. High-resolution geochemical records from cold-water corals: proxies for paleoclimate and paleoenvironmental reconstructions and the role of coral physiology. *CIESM Monograph*, 36(a):55–60, 2008.
  - [13] T. van de Flierdt, L.F. Robinson, J.F. Adkins, S.R. Hemming, and S.L. Goldstein. Temporal stability of the neodymium isotope signature of the Holocene to Glacial North Atlantic. *Paleoceanography*, 21:PA4102, doi, 2006.

- [14] C. Colin, N. Frank, K. Copard, and E. Douville. Neodymium isotopic composition of deep-sea corals from Rockall Trough : implications for past changes of hydrology during the Holocene. *AGU Fall Meeting*, 2009.
- [15] E. J. Rohling, R. Abu-Zied, C.S.L. Casford, A. Hayes, and B.A.A. Hoogakker. The Mediterranean Sea: Present and Past. *Physical Geography of the Mediterranean Basin*, 2009.
- [16] R. Margalef. From hydrodynamic process to structure (information) and from information to process. *Can. Bull. Fish. Aquat. Sci.*, 213:200–220, 1985.
- [17] J. Laborel. Marine biogenic constructions in the Mediterranean, a review. *Rep. Sci. Par natl. Port-Cros*, 13:97–126, 1987.
- [18] P. Montagna, S. Silenzi, S. Devoti, C. Mazzoli, et al. High-resolution natural archives provide new tools for climate reconstruction and monitoring in the Mediterranean Sea. *Accademia Nazionale dei Lincei*, 19(b):121–140, 2008.
- [19] S. de Villiers, G.T. Shen, and B.K. Nelson. The Sr/Ca-temperature relationship in coralline aragonite: influence of variability in (Sr/Ca) seawater and skeletal growth parameters. *Geochimica et Cosmochimica Acta*, 58:197–208, 1994.
- [20] S.J. Fallon, M.T. McCulloch, and C. Alibert. Examining water temperature proxies in Porites corals from the Great Barrier Reef. *Coral Reefs*, 22:389–404, 2003.
- [21] M. Inoue, A. Suzuki, M. Nohara, K. Hibino, and H. Kawahata. Empirical assessment of coral Sr/Ca and Mg/Ca ratios as climate proxies using colonies grown at different temperatures. *Geophysical Research Letters*, 34:doi:10.102, 2007.
- [22] A. Meibom, S. Mostefaoui, J.P. Cuif, Y. Dauphin, et al. Biological forcing controls the chemistry of reef-building coral skeleton. *Geophys. Res. Lett.*, 34:doi:10.102, 2007.
- [23] A.A. Finch and N. Allison. Mg structural state in coral aragonite and implications for the paleoenvironmental proxy. *Geophysical Research Letters*, 35:doi:10.102, 2008.
- [24] P. Montagna, M. McCulloch, M. Taviani, J. Trotter, S. Silenzi, and C. Mazzoli. An improved sampling method for coral P/Ca as a nutrient proxy. *Geochimica et Cosmochimica Acta. Goldschmidt Conference Abstracts*, A895, 25:1888–1947, 2009.
- [25] K. Tachikawa, M. Roy-Barman, A. Michard, D. Thouron, D. Yeghicheyan, and C. Jeandel. Neodymium isotopes in the Mediterranean Sea: Comparison between seawater and sediment signals. *Geochimica et Cosmochimica Acta*, 68:3095–3106, 2004.

- [26] R.L. Rutberg, S.R. Hemming, and S.L. Goldstein. Reduced North Atlantic Deep Water flux to the glacial Southern Ocean inferred from neodymium isotope ratios. *Nature*, 405:935–938, 2000.
- [27] A.M. Piotrowski, S.L. Goldstein, S.R. Hemming, and R.G. Fairbanks. Intensification and variability of ocean thermohaline circulation through the last deglaciation. *Earth and Planetary Science Letters*, 225:205–220, 2004.
- [28] A.M. Piotrowski, S.L. Goldstein, S.R. Hemming, and R.G. Fairbanks. Temporal relationships of carbon cycling and ocean circulation at glacial boundaries. *Science*, 307:1933–1938, 2005.
- [29] D. Vance, A.E. Scrivner, P. Beney, M. Staubwasser, G.M. Henderson, and N.C. Slowey. The use of foraminifera as a record of the past neodymium isotope composition of seawater. *Paleoceanography*, 19, 2004.
- [30] E.E. Martin and H.D. Scher. Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad news and good news. *Earth and Planetary Science Letters*, 220:25–39, 2004.
- [31] T. van de Flierdt, L.F. Robinson, and J.F. Adkins. Deep-sea coral aragonite as a recorder for the neodymium isotopic composition of seawater. *Geochimica et Cosmochimica Acta*, 74:6014–6032, 2010.
- [32] K. Copard, C. Colin, E. Douville, A. Freiwald, G. Gudmundsson, B. De Mol, and N. Frank. Nd isotopes in deep-sea corals in the North-eastern Atlantic. *Quaternary Science Reviews*, 29:2499–2508, 2010.
- [33] A.E. Scrivner, D. Vance, and E.J. Rohling. New neodymium isotope data quantify Nile involvement in Mediterranean anoxic episodes. *Geology*, 32:565–568, 2004.
- [34] C. Jeandel, T. Arsouze, F. Lacan, J.C. Dutay, N. Ayoub, and P. Téchiné. Nd isotopic compositions and concentrations of the lithogenic inputs into the ocean: a compilation, with an emphasis on the margins. *Chemical Geology*, 239:156–164, 2007.
- [35] P. Montagna, S. Goldstein, M. Taviani, and N. Frank. Neodymium isotopes in biogenic carbonates from the Mediterranean Sea: reliable archives of water mass circulation. *GEOTRACES Mediterranean workshop. 4-6 October 2010, Nice, France*, 2010.
- [36] B. Hönisch and N.G. Hemming. Ground-truthing the boron isotope paleo-pH proxy in planktonic foraminifera shells: partial dissolution and shell size effects. *Paleoceanography* doi:10.1029/2004PA001026, 19:2499–2508, 2004.
- [37] H. Kakihana, M. Kotaka, S. Satoh, M. Nomura, and M. Okamoto. Fundamental studies on the ion-exchange of boron isotopes. *Bull. Chem. Soc. Jpn*, 50:158–163, 1977.

- [38] A. Vengosh, Y. Kolodny, A. Starinsky, A.R. Chivas, and M.T. McCulloch. Co-precipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochimica et Cosmochimica Acta*, 55:2901–2910, 1991.
- [39] N.G. Hemming and G.N. Hanson. Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta*, 56:537–543, 1992.
- [40] A. Sanyal, N.G. Hemming, G.N. Hanson, and W.S. Broecker. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature*, 373:234–236, 1995.
- [41] G. Foster. Seawater pH, pCO<sub>2</sub> and [CO<sub>2</sub>–3 ] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271:254–266, 2008.
- [42] B. Hönlisch, N.G. Hemming, D. Archer, M. Siddall, and J.F. McManus. Atmospheric Carbon Dioxide Concentration Across the Mid-Pleistocene Transition. *Science*, 324:1551–1554, 2009.
- [43] B. Hönlisch, N.G. Hemming, A.G. Grottoli, A. Amat, G.N. Hanson, and J. Bijma. Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects. *Geochimica et Cosmochimica Acta*, 68:3675–3685, 2004.
- [44] S. Reynaud, N.G. Hemming, A. Juillet-Leclerc, and J.P. Gattuso. Effect of pCO<sub>2</sub> and temperature on the boron isotopic composition of the zooxanthellate coral *Acropora* sp. *Coral Reefs*, 23:539–546, 2004.
- [45] G. Wei, M.T. McCulloch, G. Mortimer, W. Deng, and L. Xie. Evidence for ocean acidification in the Great Barrier Reef of Australia. *Geochimica et Cosmochimica Acta*, 73:2332–2346, 2009.
- [46] Y. Liu, W. Liu, Z. Peng, Y. Xiao, et al. Instability of seawater pH in the south China sea during the mid-late Holocene: evidence from boron isotopic composition of corals. *Geochimica et Cosmochimica Acta*, 73:1264–1272, 2009.
- [47] D. Blamart, C. Rollion-Bard, A. Meibom, J.P. Cuif, A. Juillet-Leclerc, and Y. Dauphin. Correlation of boron isotopic composition with ultrastructure in the deep-sea coral *Lophelia pertusa*: implications for biomineralization and paleo-pH. *Geochim. Geophys. Geos.*, 8(doi:10.1029/2007GC001686), 2007.
- [48] J. Trotter, P. Montagna, M. McCulloch, S. Silenzi, S. Reynaud, G. Mortimer, S. Martin, C. Ferrier-Pagès, J.-P. Gattuso, and R. Rodolfo-Metalpa. Quantifying the pH “vital effect” in the temperate zooxanthellate coral *Cladocora caespitosa*: validation of the boron seawater pH proxy. *Earth and Planetary Science Letters*, 303:163–173, 2011.
- [49] A. Theocharis, B. Klein, K. Nittis, and W. Roether. Evolution and status of the Eastern Mediterranean Transient. *Journal of Marine Systems*, 33-34:91–116, 2002.